

CONVERSION OF WASTE POLYVINYL CHLORIDE (PVC) TO USEFUL CHEMICALS

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INTRODUCTION

Developments of recycling technologies are expected one of the most important keys for saving energy and resources, and minimization impact for environment. For instance, combustion of waste for power generation and conversion of plastics into liquid fuels have been studying for thermal energy recycling ^{1), 2)}. However, PVC has been excepted from the most of these experiments. Because, heat of combustion of PVC is almost a half of other plastics', hydrogen chloride, which is produced at low temperature, corrodes the combustion chamber, and PVC causes coking reaction during pyrolysis of plastics.

Numerous investigations have been conducted on degradation of PVC. However, most of these experiments were done to improve heat resistance of PVC ^{3), 4)} or to study reaction mechanism of PVC degradation ^{5), 6)}. Pyrolysis of PVC into liquid products have been studying since 1960's from a view of environmental protection ^{7), 8), 9)}. Recently, Y. Maezawa et al. reported PVC was converted into oil at 600 °C with sodium hydroxide ¹⁰⁾. However, more than 50 % of hydrocarbon fraction of PVC was converted to residue and gas in their experiment. We are going to develop a new technology to convert of PVC into useful chemicals or liquid fuels at high efficiency by using hydrogen donor solvent.

In this experiment, we used PVC resin, because commercial PVC contain many other compounds as stabilizer. Chlorine in PVC was removed by pretreatment to prevent corrosion of an autoclave. We liquefied pretreated PVC resin in tetralin with some catalysts.

EXPERIMENTAL

Pre treatment of PVC: PVC resin was supplied Mitsubishi Kasei Vinyl Company. The PVC resin (100 g) was charged in a Pyrex flask (300 ml) and heated with nitrogen gas flowing. The samples were heated according to following temperature program, 200 °C (24 hours), 250 °C (24 hours) and 300 °C (24 hours). Finally, the samples were heated at 300 °C for 24 hours under vacuum. Weight of samples decreased less than 40 % of initial PVC resin after the pre treatment. Elemental analyses of original PVC resin and pretreated PVC resin were shown in Table 1. The pretreated resin still contained 2.8 % of chlorine.

Reaction procedure: Pretreated PVC resin (10.0 g) and tetralin (70.0 g) were charged into a 300 ml magnetic stirred autoclave. In order to study effects of catalysts on product distribution and content of remained chlorine in products, nickel - molybdenum catalyst for upgrading of petroleum (NiMo/Al₂O₃, 1.0 g) and sulfur (0.5 g), iron oxide (Fe₂O₃, 1.0g) and sulfur (0.5 g), Zeolite for FCC (1.0 g), and fine nickel powder (Ni, 1.0 g, diameter < 0.3 μm) were added in a few experiments. All reactions were carried out at 440 °C and 470 °C under an initial pressure of 6.9 MPa of hydrogen gas or nitrogen gas. Reaction products were separated residues and liquid products by filtration. The liquid products were vacuum distilled at 330 °C for 60 min. The vacuum bottoms were separated HS (hexane soluble) and HI (hexane insoluble) by hexane extraction. The residue and extracted products, HS and HI, were dried for one day at 110 °C under vacuum and weighted.

Analysis of products: Gas products were collected into a Teflon bag through 10% of sodium hydroxide aqueous solution and analyzed by gas chromatography (GASUKURO KOGYO, GC-312, molecular sieve 5A, molecular sieve 13X, Porapak N, gasukuro 54, and VZ-7). Liquid products were analyzed by gas chromatography (CARLO ERBA INSTRUMENTS, HRGC 5300) with capillary column (HP Ultra 1, 0.2 mm, 50m). Chlorine content in product was measured by total chlorine analyzer (Mitsubishi Kasei, TOX-10Σ).

RESULTS AND DISCUSSION

Product distributions from the pretreated PVC resins were shown Figure 1. Yields of each product were obtained by using an equation shown below. Oil yields were calculated from yields of gas, HS, HI and residue.

$$\text{yield(i)} = \frac{\text{weight of product (i)}}{\text{weight of hydrocarbon fraction in chlorine removed PVC}} \times 100$$

Yields of gas and residue were only 3 % and 13 % respectively at 440°C under nitrogen gas. Y. Maezawa et al.¹⁰⁾ reported that more than 50 % of hydrocarbon fraction in PVC was converted to gas and residue under conventional pyrolysis condition with sodium hydroxide. Remarkable decreases of yields of gas and residue observed in our experiment were caused by using hydrogen donor solvent. Product distribution from pretreated PVC indicates that hydrogen gas and NiMo/Al₂O₃ catalyst enhanced conversion of HS to oil and residue to HI at 440 °C. However, decomposition of HI to HS was not promoted in spite of presence of hydrogen gas and NiMo/Al₂O₃ catalyst. Yields of oil and HS increased with temperature significantly. Oil yield and HS yield were achieved to 40 % and 44 % respectively at 470 °C with NiMo/Al₂O₃ under hydrogen gas.

Methane, ethane, propane were produced mainly under our reaction condition. Production of methane increased particularly at 470 °C. Benzene, toluene and xylene (BTX) were produced as main liquid products from the pretreated PVC. Total yields of BTX were shown in Figure 2. Yields of these products increased with temperature significantly under hydrogen gas. These trends imply hydrogen gas enhanced production of BTX from pretreated PVC. Tetralin isomer, alkylated tetralin and tetralin dimmer were observed in the solvent after liquefaction. Productions of these compounds indicate hydrogen was transferred from tetralin very rapidly, isomerization and dimerization of tetralin radical were enhanced.

In order to show effects of various catalysts on pyrolysis of pretreated PVC, NiMo/Al₂O₃, iron oxide (Fe₂O₃), Zeolite and fine nickel powder were used. Product distributions of these catalysts were shown in Figure 3. Remarkable increases of oil yield or HS yield were not observed at 440°C. The NiMo/Al₂O₃ was most effective catalyst for pyrolysis of pretreated PVC.

Low chlorine contents of products are very important to use them as chemicals and liquid fuels. Chlorine contents of products from liquefaction were shown Figure 4. Chlorine contents of oil and vacuum bottom (HI+HS) were 25 ppm and 8 ppm respectively under nitrogen gas at 440 °C. These results show 99.9% of chlorine in pretreated PVC was removed by liquefaction. Chlorine contents of oil and HS+HI produced under hydrogen gas were lower than that of products obtained under nitrogen gas. Under hydrogen gas with NiMo/Al₂O₃, chlorine content of oil and HS+HI were only 2 ppm and 3 ppm respectively. Remarkable decreases of chlorine content were observed at 470 °C. Chlorine content decreased with severity of hydrogenation of products. These results imply chlorine was removed by hydrogenation reaction of products.

Effects of catalysts on chlorine content of HS+HI were shown in Figure 5. Iron oxide and fine nickel powder did not show remarkable effects on removal of

chlorine in products. On the other hand, zeolite inhibited removal of chlorine from products. This negative effect was estimated to be caused by strong acidity of zeolite.

SUMMARY AND CONCLUSION

PVC was heated under nitrogen gas to remove chlorine at 300 °C for 24 hours. Then, pretreated PVC was liquefied in tetralin at 440 °C and 470 °C for 60 minutes under an initial pressure of 6.9 MPa of hydrogen gas and nitrogen gas. Oil yield and HS yield were 40 % and 44 % respectively at 470 °C with NiMo/Al₂O₃ under hydrogen gas. Benzene, toluene and xylene were produced as main liquid product. Chlorine content in products decreased with temperature. Less than 3 ppm of chlorine was retained in oil and vacuum bottom (HS+HI) at 470 °C under hydrogen gas with NiMo/Al₂O₃. Hydrogen transferred from tetralin and hydrogen gas enhanced conversion of pretreated PVC to liquid products and removal of chlorine from products.

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Table 1 Elemental analyses of PVC and pretreated PVC

	C	H	O	Cl	H/C	O/C	Cl/C
PVC (resin)	38.64	4.81		56.53 ¹⁾	1.48		0.50
Pretreated PVC (300°C)	85.99	7.10		2.84	0.98		0.01

1) calculated (100 - C% - H%)

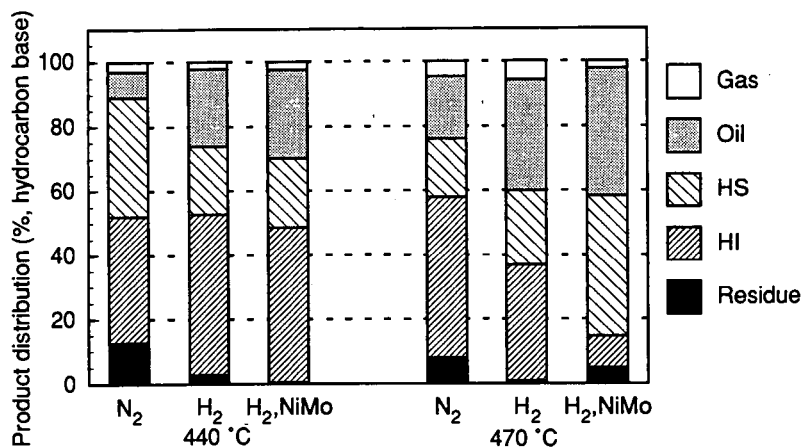


Figure 1 Distribution of products from pretreated PVC.

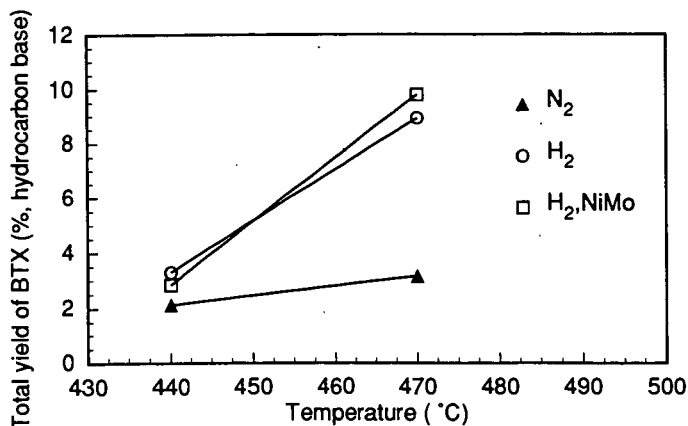


Figure 2 Total yield of benzene, toluene and xylene from pretreated PVC.

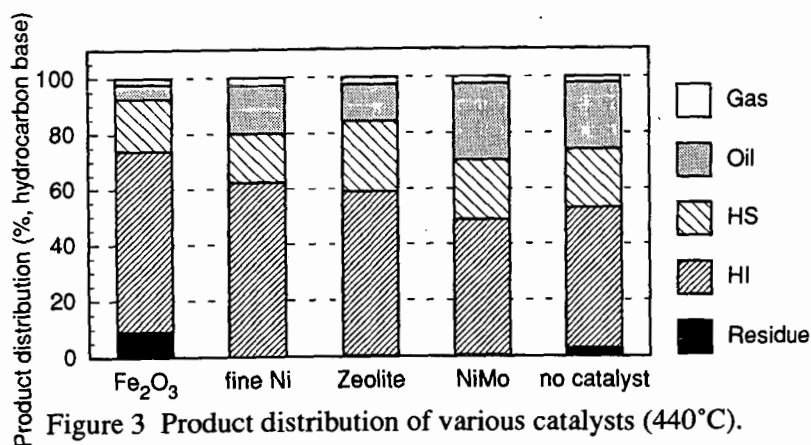


Figure 3 Product distribution of various catalysts (440°C).

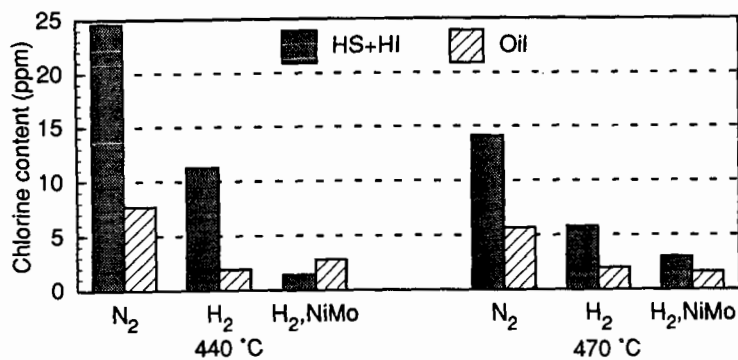


Figure 4 Chlorine content of oil and vacuum bottom (HS+HI).

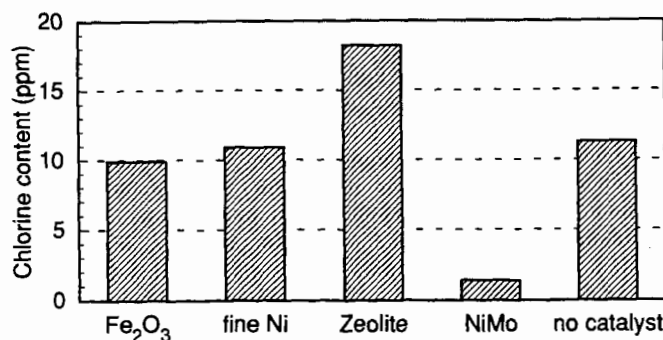


Figure 5 Effect of catalysts on chlorine content of vacuum bottom (HS + HI).